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INTERIM REPORT

on

ELECTRICAL CONDUCTION AND THERMIONIC EMISSION IN SEMI-CONDUCTORS

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Studies of the electrical properties of single crystals of pure oxide have been made in only a few cases. The interest in thorium oxide arises largely from its application as a thermionic emitter and also from the fact that optically clear, homogeneous, crystalline specimens are available.

This report is a brief statement of our experimental work pertaining to the conduction mechanism in thorium oxide. The material to be described is primarily that which involves electronic conduction. Certain ionic and electrolytic effects have been previously reported and will only be mentioned here in cases where they intrude themselves in a manner which cannot be ignored. The data to be reported are concerned with conductivity and thermo-electric power in atmospheres of various gases and in vacuum. The temperature range of the present data is between 650° and 1000° centigrade.

It has been found that the presence or absence of oxygen atmosphere has a pronounced effect, both upon the electrical properties of a crystal, and upon its color. As previously reported, a thoria crystal heated in oxygen at 1000° C will be a deep red in color. If the oxygen is then pumped out leaving a vacuum, the temperature remaining the same, the crystal will bleach to a colorless condition. The same bleaching will also occur if the oxygen be replaced by hydrogen or by helium. Weight measure-

ments with a microbalance have shown that the density of oxygen atoms responsible for the color change must be less than 10^{18} per cc.

The effect of this change of oxygen content upon the conductivity is shown in Figure 1.

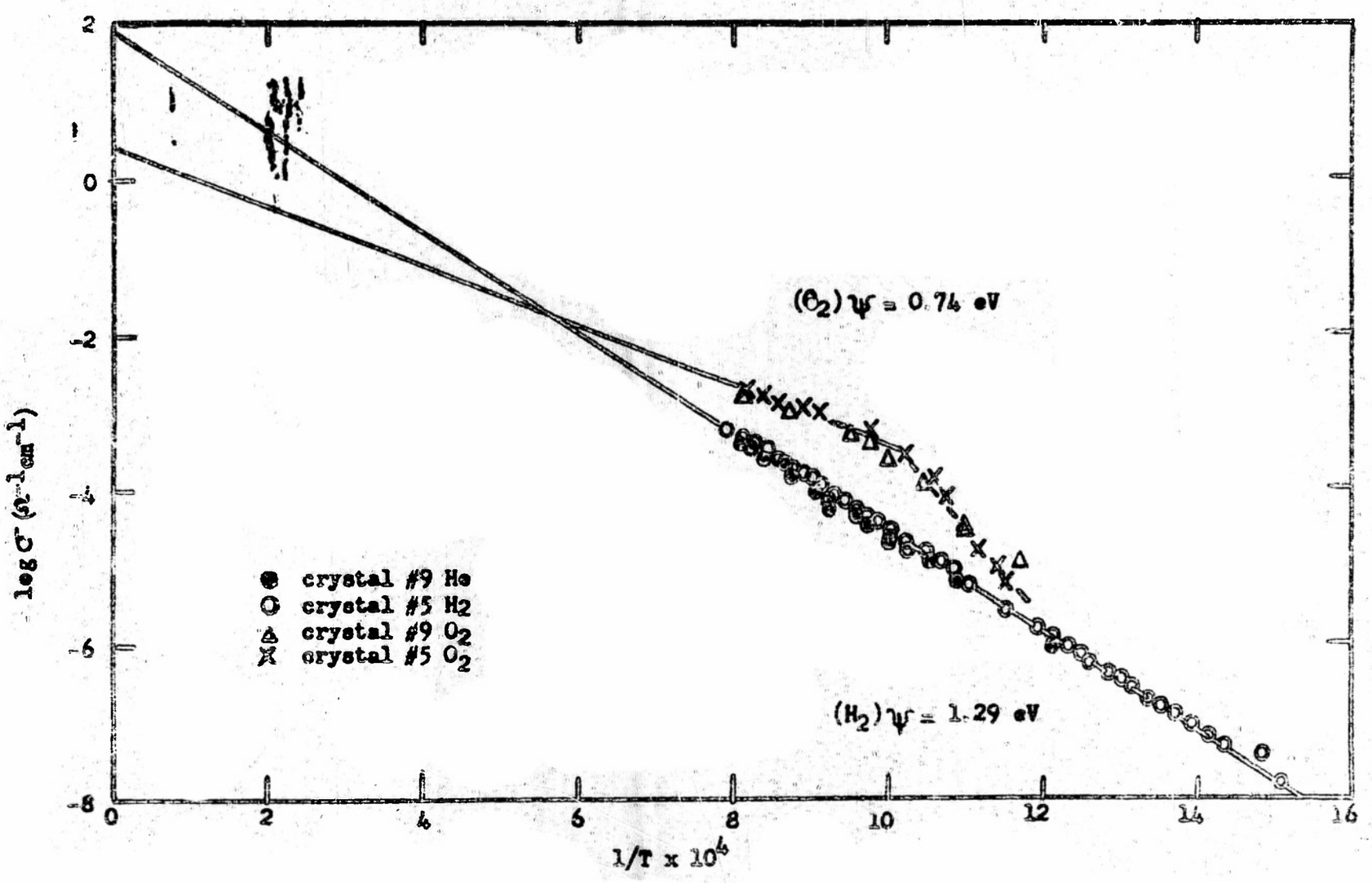
The lower curve in this diagram shows results obtained in an atmosphere of hydrogen or helium. They were made on different crystals. Measurements taken in vacuum on a third crystal lie somewhat below the line but still fairly close to it.

It seems, therefore, that the conduction in the absence of oxygen is not markedly dependent upon the atmosphere.

The addition of oxygen, however, increases the conductivity by a factor of the order of 10. In the high temperature region the results are nicely reproducible; values taken with a dozen crystals agree within about 10 percent. A break of slope occurs at about 1000° K and at lower temperatures the measurements become progressively more difficult on account of the time required for the system to come to equilibrium.

The time required for the conductivity to reach a new equilibrium when the atmosphere is changed from oxygen to non-oxygen, or vice versa, is quite rapid at temperatures around 1100° K; the new value is attained in a few seconds. In the 700° K region the time required will be many minutes. Quantitative consideration of these time-phenomena in terms of probable diffusion coefficients

Figure 1. Effect of Oxygen Content Upon Conductivity



remains to be done.

Application of semi-conductor theory to these data would require mobility data which are not available. Using mobility values for copper oxide, however, density of impurity centers is of the order of 10^{16}. This is based upon the slope of the high temperature portion of the oxygen curve.

A similar calculation carried out for the non-oxygen curve will involve a higher value of the energy gap, and, accordingly, a higher density of centers of the order of 10^{18}.

As stated earlier, the conductivity values from crystal to crystal show fair reproducibility, of the order of 10 percent. Values of slope however show a scatter also of the order of 10 percent and this is, of course, reflected in a high degree of uncertainty in the calculated density of impurity centers.

The elementary semi-conductor theory postulates a density of centers which is independent of temperature. In the case of a solid immersed in an atmosphere of a gas whose nature is pertinent to the activation, this assumption is doubtful to say the least.

In the case of the non-oxygen curve, the similarity of data when using hydrogen or helium or vacuum indicates that neither hydrogen nor helium have a part in the creation of impurity centers and the calculated value of this quantity probably has some meaning when oxygen is not present.

With an oxygen atmosphere, however, it appears that dissolved oxygen must play an essential role in the conductivity mechanism. It seems certain therefore that, for this case, a calculation of the density of centers, based upon the assumption that this quantity is independent of temperature, is quite meaningless.

In this connection, Mr. Weinreich has carried out measurements of the dependence of conductivity upon oxygen pressure. Some data regarding this are shown in Figure 2.

The lowest curve shows data taken in vacuum. The two upper curves correspond to two different pressures of oxygen surrounding the specimen. Non-conformity to the elementary theory is immediately evident from the fact that the intercept, and accordingly the density of centers which would be computed, is a decreasing function of the oxygen pressure.

The functional relation between conductivity and pressure is sometimes derived by considering an equilibrium reaction equation, involving charge carriers, vacancies, etc., and applying the Law of Mass Action. If we assume that we are dealing with p-type conduction involving vacancies produced by the removal of quadruply-ionized thorium, we arrive at a pressure-to-the 1/5th-power law. Figure 3 shows data regarding this functional relation. We see that the experimental exponents are somewhat smaller than 1/5th. It may perhaps be hazarded that this points to the degree of ionization in the thorium oxide crystal being less than the value of 4 which corresponds to its valence.

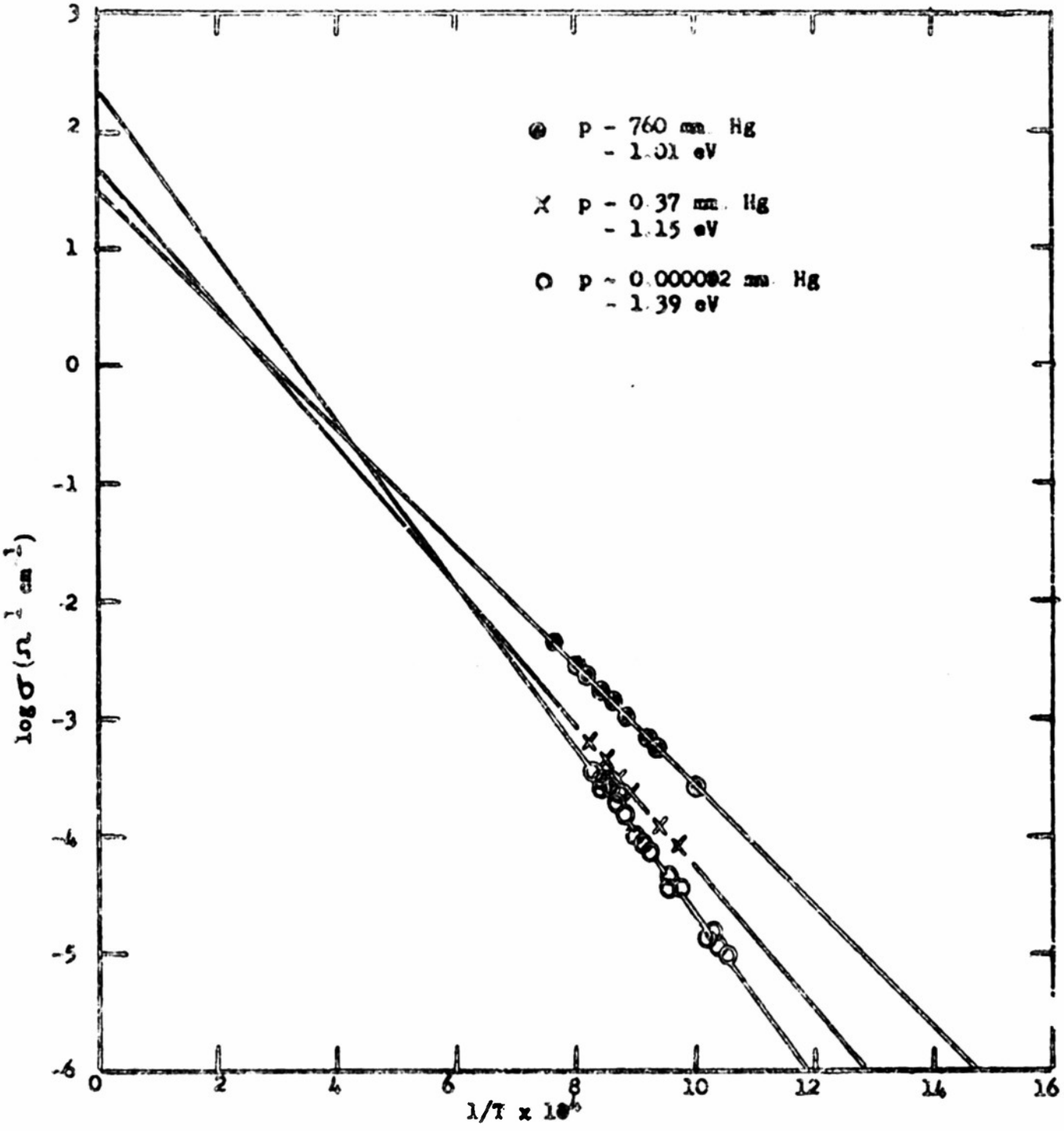
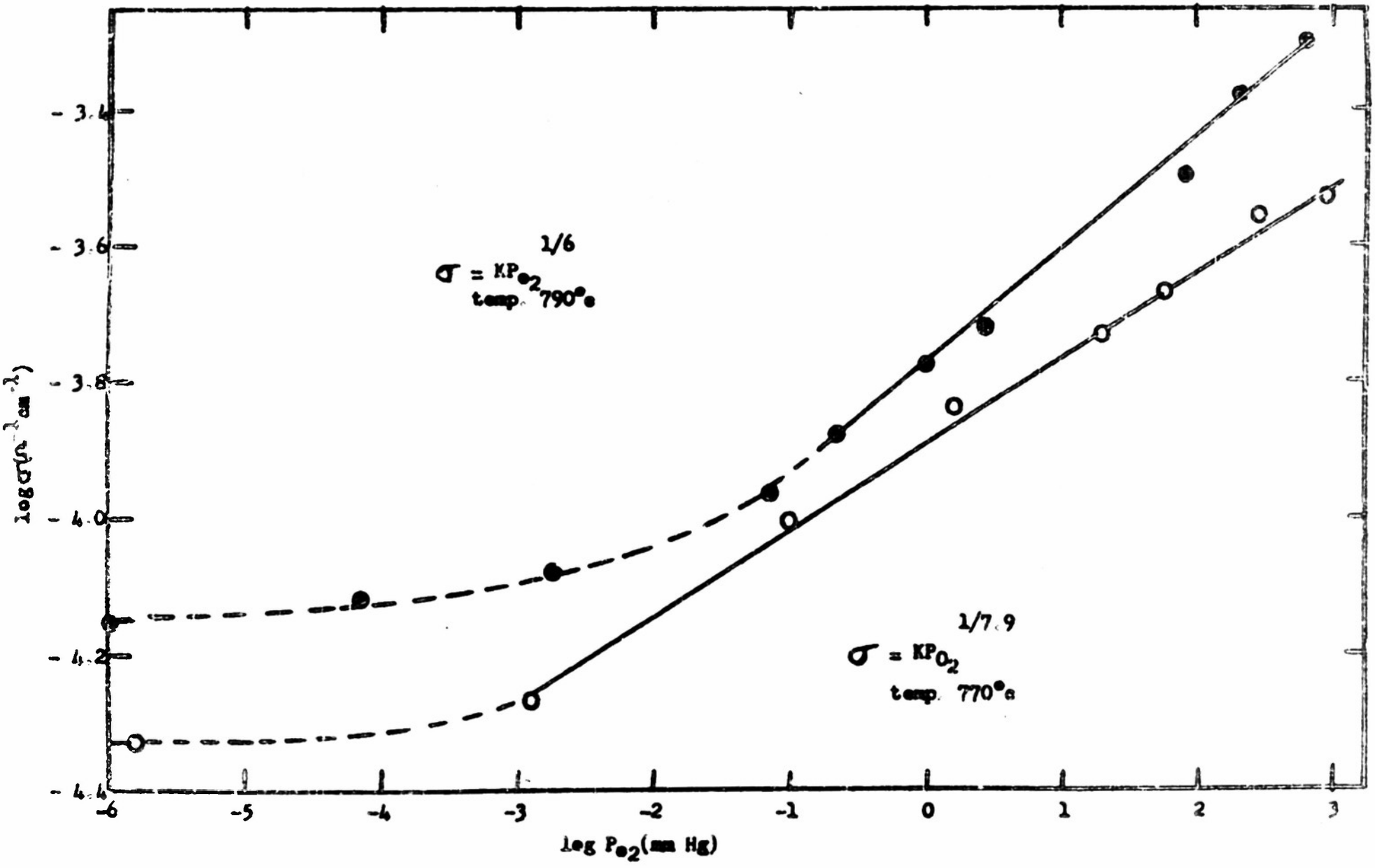


Figure 2. Dependence of Conductivity Upon Oxygen Pressure

Figure 3. Functional Relation Between Conductivity and Pressure

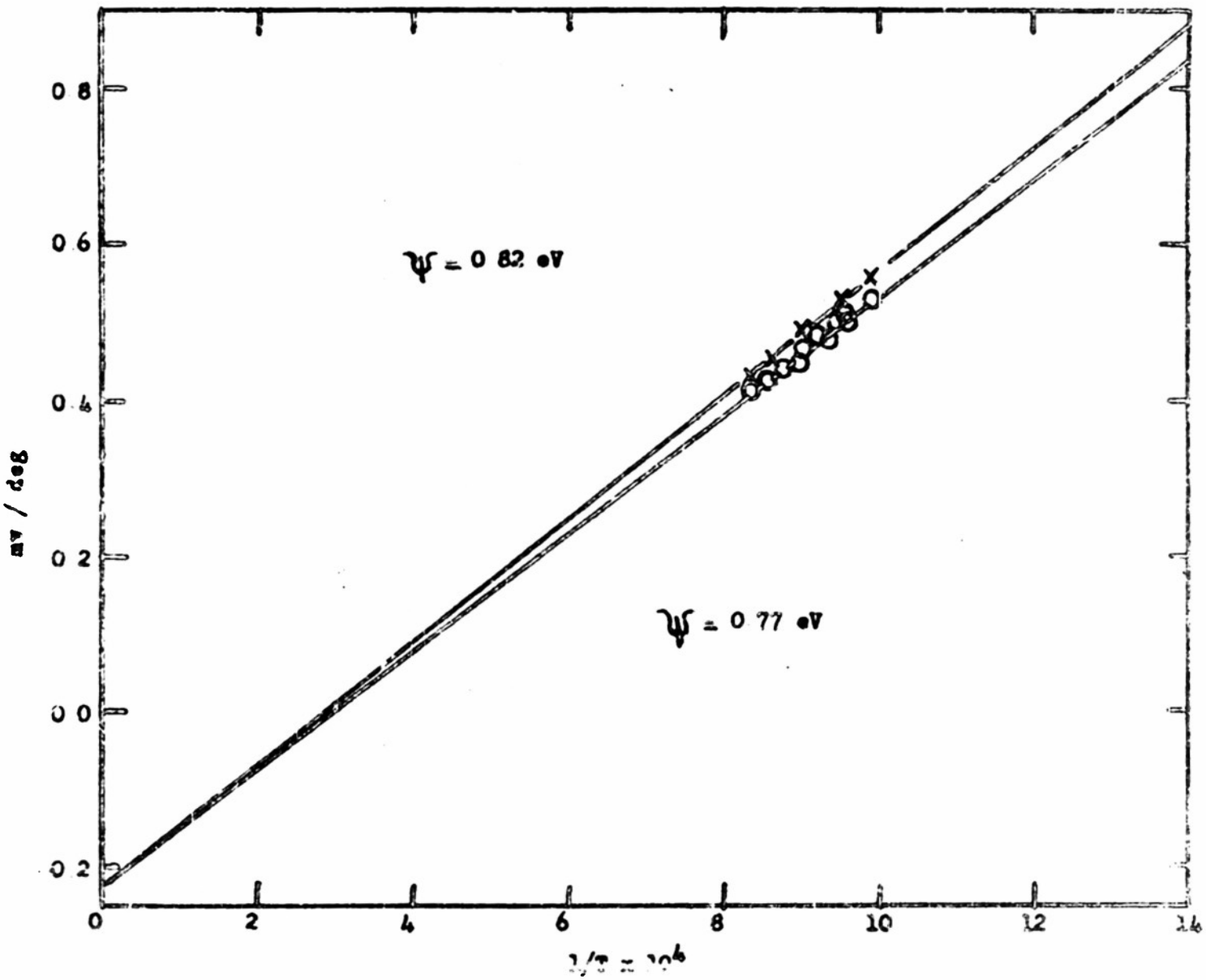


The hypothesis of p-type conduction is supported by the sign of the Seebeck effect. Measurements of thermo-electric power have also been attempted in various atmospheres. Reproducible data are obtainable in oxygen, but in the non-oxygen case the reversible thermal effect is very difficult to disentangle from polarization effects which give a complex pattern of time-dependent phenomena. It is possible to observe, however, that when one changes from the oxygen case to the non-oxygen case, the sign of the Seebeck voltage changes in the sense that p-type conduction is indicated in the presence of oxygen and n-type in hydrogen or vacuum.

Figure 4 shows data from two different runs using the same crystal of thorium oxide. Thermo-electric power is plotted against reciprocal temperature. If the elementary theory were valid, one could compute from these curves, just as from conductivity curves, the energy gap and the density of impurity centers. As a matter of fact, one intriguing thing was the agreement of gap-values as deduced from the two kinds of measurement. Just as with conductivity, however, it seems definitely erroneous to assume for the oxygen case, that the density of centers remains constant as the temperature varies. If this assumption is made, the computed density turns out to be unreasonably large, of the order of 10^{24}.

On the assumption that the simplest semi-conductor model is pertinent, equations for conductivity σ and thermo-electric power $\frac{dV}{dT}$ are respectively (1, and (2).

Figure 4. Thermo-electric P[illegible] of Thorium Oxide in an Atmosphere of Oxygen



$$\sigma = 2 e v n_o^{1/2} \left(\frac{2\pi m k}{h^2} \right)^{3/4} T^{3/4} e^{\frac{-E/2}{kT}} \qquad (1)$$

$$\frac{dV}{dT} = \frac{k}{e} \left[2 + \frac{1}{2} \log \frac{(2\pi m k T)^{3/2}}{n_o h^3} + \frac{E/2}{kT} \right] \qquad (2)$$

If one could postulate that the density of impurity centers has a temperature dependence of the form:

$$n_o = e^{\alpha - \frac{\beta}{kT}} \qquad (3)$$

The above equations would become

$$\sigma = 2 e v e^{\frac{\alpha}{2}} \left(\frac{2\pi m k}{h^2} \right)^{3/4} T^{3/4} e^{\frac{-E/2 + \beta/2}{kT}} \qquad (4)$$

$$\frac{dV}{dT} = \frac{k}{e} \left[2 - \frac{\alpha}{2} + \frac{1}{2} \log \left(\frac{2\pi m k}{h^2} \right)^{3/2} T^{3/2} + e^{\frac{E/2 + \beta/2}{kT}} \right] \qquad (5)$$

One sees that uniformity of slope is preserved; the equality of gap-values, calculated assuming (1) and (2) to be valued, would also obtain with (4) and (5) although the value so calculated would be incorrect.

Besides accounting for the equality of slopes, the assumption (3) can also give reasonable density of impurity centers.

This assumption, however, requires that the density n_o be an increasing function of temperature. If the process be one of solution of oxygen in the crystal, decreasing function would be more admissible intuitively. However, if thermally produced lattice defects are a factor in the generation of the donor centers, an increasing function might be possible. These matters will receive further consideration.

A determination of the temperature dependence of n_o would be the next topic on this aspect of the program. It should obviously have precedence over any attempts to explain the results by more complicated semi-conductor mechanisms.

Plans for the Future.

It is felt that the thermo-electric effects have received sufficient attention for the time being. X-ray diffraction investigation of the different color forms of thorium oxide are planned. Further studies of the causes of the red coloration are in order. Three such causes are known: oxygen absorption, u. v. radiation, and flow of current in a gas other than hydrogen.